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(54) **USE OF HYDROPHILIC SILICONES AS DENTAL IMPRESSION MATERIALS**
VERWENDUNG HYDROPHILER SILIKONE ALS ZAHNABDRUCKMATERIALIEN
UTILISATION DE SILICONES HYDROPHILES POUR DES IMPRESSIONS DENTAIRES

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- **CHEMICAL ABSTRACTS, Volume 106, 1987, (Columbus, Ohio, US), B.K. NORLING: "Surface Wettability Modification of Poly (Vinylsiloxanes) with Nonionic Surfactants", see Abstract 23242b, & Journal of Celloids Surf. 1986, 20 (4), pages 277-288**

Remarks:
The file contains technical information submitted after the application was filed and not included in this specification

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Description

Technical Field

[0001] This invention relates to the use as a dental impression material for vulcanizable silicone compositions.

Background Art

[0002] Many different substances have been used as dental impression materials, each having its own advantages and disadvantages. An impression material must undergo a transformation, while in the mouth, from a viscous liquid to a rubbery solid. While factors such as taste, odor, toxicity, viscosity, cure speed, ease of demolding and strength after cure are all important, accuracy is of paramount concern. An impression material must accurately replicate the shape, size, and relative locations of both hard and soft tissues within the mouth. After cure, the impression must enable casting ("pouring") of an accurate model. The model usually is a plaster of Paris "stone" prepared from an aqueous gypsum slurry, which after setting represents a positive mold of the mouth. In recent years, silicones of both the condensation cure and addition cure varieties have become widely used as impression materials. They exhibit very good accuracy, together with an absence of taste and odor, easy demolding and other properties generally equivalent to or better than other commonly-used impression materials. However, silicone impression materials suffer from the disadvantage of hydrophobicity. This causes inaccurate impressions in moist fields, and discourages thorough wetting and accurate replication when the model is poured. In an attempt to provide better wetting of the impression by the gypsum slurry, some dental laboratories spray the cured impression with a detergent solution just prior to pouring the model. Lacy, A., Treleaven, S. and Jendresen, M., "The Effect of Selected Surfactants on the Wetting Behavior of Gypsum Die Stone on Impresion Materials", Cal. Dent. Assn. J., 5:36-40 (1977) and Norling, D.K. and Reisbick, M.H., "The Effect of Nonionic Surfactants on Bubble Entrapment in Elastomeric Impression Materials", J. Pros. Dent., 42:342-347 (Sept., 1979) both describe curable silicone compositions containing certain nonionic hydrocarbon surfactants and their use in dentistry.

[0003] Repeated attempts have also been made to render silicones more hydrophilic by chemically modifying the siloxane backbone or by appending to the backbone various functional groups. Typical approaches are described in U.S. Patent Nos. 4,259,467 (and in many of the references cited therein) and 4,332,922.

[0004] Siloxanes have been used as surface active agents, emulsifiers, defoamers or coatings, see, e.g. U.S. Patent Nos. 3,057,901, 3,398,104, 3,402,192, 3,505,377, 3,560,544, 3,929,509, 3,980,688, 4,160,776, 4,226,794, 4,337,168, 4,395,454, 4,414,660, 4,431,789, 4,468,491, 4,510,227, 4,517,240 and Re 25,727. Other publications describing the properties of siloxanes include "Silwet^R Surface Active Copolymers" (product literature from Union Carbide Corp., dated October, 1983), "Organomodified Oils [OMO]" (product literature from Union Carbide Corp., dated April, 1982), "UCARSIL^R EPS Silicone Hydrophilic Finish" (product literature from Union Carbide Corp., dated March, 1984), "Silicate Cluster™ Fluids (product literature from Olin Corp.), and Vick, S.C., "Structure/Property Relationships for Silicone Polyalkyleneoxide Copolymers and Their Effects on Performance in Cosmetics", Soap/Cosmetics/chemical Specialties, 60 (5), 36 (May, 1984).

[0005] U.S. Patent No. 4,354,873 describes an antifouling coating for application to submerged boat hulls. The coating contains fumed silica, silicone oil, antifoulant, and an anionic, nonionic or amphoteric surfactant.

[0006] US-A-4,144,206 discloses high temperature curable silicone resins in which polyether components may give hydrophilicity but there is no disclosure of room temperature resins in the context of dental impression compositions nor would the amounts of surfactant present be sufficient to give the hydrophilicity as mentioned by the three minute water contact angle test of the present application. This is also true of other somewhat similar documents such as DE-A-2,922,295, US-A-4,477,626 and GB-A-1,155,741.

Disclosure of Invention

[0007] The present invention provides for the use as a dental impression material of a curable room temperature vulcanizing silicone composition said composition comprising a mixture of (a) curable silicone prepolymer and (b) surfactant selected from the group consisting of (i) ethoxylated nonionic surface active agents containing one or more siloxane or perfluoroalkyl solubilizng groups and (ii) cationic or amphoteric fluorochemical surface active agents, in which, when the surfactant is a cationic surfactant, it contains at least one cationogenic group which is the radical of a base having an ionization constant in water at 25°C of at least about 10^{-6}, and, when it is an amphoteric surfactant, it contains at least one such cationogenic group and also at least one anionogenic group which is the radical of an acid having an ionization constant in water at 25°C of at least about 10^{-6}, said surfactant being present in sufficient amount and said ethoxylated nonionic surface active agent, if present, containing sufficient ethyleneoxy groups so that said composition, when cured, has a three minute water contact angle below 65°, and said surfactant being capable of migration throughout the cured silicone composition and into adjacent fluids.

[0008] The cured composition is readily wet by water, yet retains the other desirable properties characteristic of silicones. The use of this composition facilitates the making of accurate dental impressions and the pouring of accurate models.

[0009] Dental impressions are made by forming a negative model of oral tissue using such a composition.

Detailed Description

[0010] In the practice of the present invention, the curable silicone composition can be a one-part or muliple-part composition cured by the presence of adventitious moisture, crosslinking agents, and catalysts. Most preferred are two-part addition cure or condensation cure compositions of the room temperature vulcanizing ("RTV") variety. The composition contains a "curable silicone prepolymer", that is, a polysiloxane having one or more functional groups which enable the prepolymer to be polymerized or cured to a state of higher molecular weight. Suitable silicone prepolymers are well-known in the art and are described, for example, in "Silicones", Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., 20, 922-962 (1982).

[0011] The surfactants used in the present invention are selected from certain ethoxylated nonionic surface active agents (for brevity, these will sometimes be referred to hereafter as "ethoxylated surfactants") and certain fluorochemical surface active agents (for brevity, these will sometimes be referred to hereafter as "fluorosurfactants"). Included among the surfactants useful in the present invention are ethoxylated nonionic surfactants containing perfluoroalkyl groups. These could be called ethoxylated surfactants or fluorosurfactants. They will be referred to herein as "ethoxylated surfactants", and the term "fluorosurfactants" will be used to refer to the remaining fluorochemical surfactants used in the present invention. Such fluorosurfactants are cationic or amphoteric fluorosurfactants.

[0012] The surfactant contains one or more solubilizing groups (e.g., one or more siloxane groups or perfluoroalkyl groups) which render the surfactant soluble or dispersible in the silicone prepolymer. The surfactant also contains one or more water-loving groups which render a cured composition of the invention hydrophilic. When the surfactant is an ethoxylated surfactant, the water-loving groups are ethyleneoxy ($-C_2H_4O-$) groups or hydroxyalkyl-substituted ethyleneoxy (e.g., $-CH_2CH(CH_2OH)O-$) groups. For brevity, these water-loving groups will sometimes be collectively referred to hereafter as "ethyleneoxy" groups. When the surfactant is a fluorosurfactant, the water-loving groups are cationic groups or amphoteric groups, as described in more detail below.

[0013] The surfactant is present in a sufficient amount (and if it is an ethoxylated surfactant, it contains a sufficient number of ethyleneoxy groups) so that the silicone composition, when cured, has a three minute water contact angle below about 65°. The term "three minute water contact angle" refers to the contact angle formed by a drop of distilled water three minutes after it is applied to a cured composition of the invention, as measured at room temperature using a goniometer. Such contact angle measurements can be made as described in Noll. W., "Chemistry and Technology of Silicones", 447-452 at 448 (1982). Preferably, such measurements are conducted by curing a composition of the invention against a smooth substrate (e.g., a glass sheet), separating the substrate and silicone after cure, and placing the water drop on the smooth cured surface of the silicone. Preferably, the compositions of the invention have a three minute water contact angle below about 45°, more preferably below about 30°, and most preferably below about 10°.

[0014] The measured contact angle appears to be strongly dependent upon the amount of surfactant and, when the wetting agent is an ethoxylated surfactant, the number of ethylenoxy groups present within the surfactant. In general, as the amount of surfactant increases, the water contact angle decreases. In general, as the number of ethyleneoxy groups in an ethoxylated surfactant increases beyond one, the water contact angle decreases to a minimum and then increases. The number of ethyleneoxy groups which provides the desired three minute water contact angle will vary depending upon several other factors, including the remaining substituent groups present in the ethoxylated surfactant. The effect of such other factors is illustrated in the examples set forth below. For example, the water contact angle tends to increase if propyleneoxy groups are present in the ethoxylated surfactant. Preferably no propyleneoxy groups are present in such surfactant.

[0015] It has also been found that the measured water contact angle increases if a cured composition is immersed in running water for a prolonged period of time. Without intending to be bound by theory, it is believed that the surfactant is dissolved or dispersed throughout the cured silicone compositions of the invention and can migrate therein and into adjacent fluids. When a drop of water is placed on a cured composition of the invention, it is believed that the surfactant migrates into the drop and reduces the interfacial surface tension between the water and the silicone. This hypothesis is supported by the above-noted increase in water contact angle after prolonged water exposure, and by two additional observations. First, the measured water contact angle slowly changes after the drop is placed on the surface of the cured silicone, generally reaching an equilibrium after about five minutes. Second, if the drop is observed using an optical comparator (which provides a highly magnified view of the drop), schlieren patterns become visible at the interface between the drop and the silicone within a few seconds after the drop is applied. As this takes place, the schlieren patterns diffuse throughout the drop and the drop slowly collapses and spreads out on the surface of the silicone.

[0016] In view of the above the use of the cured compositions perhaps is best regarded as making use of semiper-

manent hydrophilicity, that is, the hydrophilicity which is subject to diminution upon prolonged contact with water. This dimunition is not a material drawback when making dental impressions, since the amount of water or other fluids which will come into contact with the impression is not excessive and in any event somewhat predictable in advance.

[0017] Turning now to a more detailed discussion of the ethoxylated surfactant, the ethyleneoxy group(s) can be attached to the solubilizing group through either end of an ethyleneoxy group, that is, through a carbon atom or an oxygen atom of the ethyleneoxy group. Although the ethoxylated surfactant can contain as little as one ethyleneoxy group, preferably it contains at least three such groups, more preferably about five to fifteen such groups. The number of ethylenoxy groups should not be so large that the ethoxylated surfactant becomes waxy, as that may reduce its effectiveness. The ethoxylated surfactant also can contain other groups or substituents, if present in types and amounts which do not interfere with the functioning of such surfactant in the present invention or with the curing of the silicone prepolymer. Examples of such groups include propyleneoxy ($-C_3H_6O-$), vinyl, $-NH_2$, -SH and oxirane groups.

[0018] The ethyleneoxy groups are preferably bonded to one another in series, and can be terminated with a hydrogen atom, an alkyl group, one or more propyleneoxy groups, or a solubilizing group of the type described above.

[0019] A preferred class of ethoxylated surfactants containing a siloxane solubilizing group has the average formula

$$R-\underset{R}{\overset{R}{|}}SiO\left[\underset{R}{\overset{R}{|}}SiO\right]_x\left[\underset{R^1O(C_2H_3R^2O)_a(C_3H_6O)_bR^3}{\overset{R}{|}}SiO\right]_y\underset{R}{\overset{R}{|}}Si-R \qquad \mathrm{I}$$

where each R is independently a monovalent hydrocarbyl radical, R^1 is a divalent hydrocarbylene radical, each R^2 is independently hydrogen or a lower hydroxyalkyl radical, R^3 is hydrogen or a monovalent hydrocarbyl radical, x and b are independently greater than or equal to zero, and y and a are independently greater than or equal to one, with the proviso that a has a sufficient value and b is small enough so that a cured composition of the invention has the desired three minute water contact angle. Preferably in compounds of Formula I, R and R^3 are $-CH_3$, R^1 is $-C_3H_6-$, R^2 is hydrogen, x is zero or one, y is one to five, a is five to 20 and b is zero.

[0020] Another preferred class of ethoxylated surfactants has the average formula

$$RSi\left[(O\underset{R}{\overset{R}{|}}Si)_x(OC_2H_3R^2)_a(OC_3H_6)_bOR^3\right]_3 \qquad \mathrm{II}$$

where R, R^2, R^3, x, a and b are as defined above. Preferably in compounds of Formula II, R and R^3 are $-CH_3$, R^2 is hydrogen, a is five to 20 and b is zero.

[0021] Ethoxylated surfactants of Formulas I and II above are described in the above-mentioned Union Carbide Corp. product literature and in U.S. Patent Nos. 3,505,377, 3,980,688, and 4,431,789. Several of such ethoxylated surfactants are available from Union Carbide Corp. as "SILWET" surface active copolymers. Preferred SILWET surface active copolymers include SILWET L-77, L-7600 and L-7602. SILWET L-77 is an especially preferred ethoxylated surfactant. It is believed to have Formula I above, where R and R^3 are $-CH_3$, R^1 is $-C_3H_6-$, R^2 is hydrogen, x is zero or one, y is one or two, a is about seven and b is zero.

[0022] An additional preferred class of ethoxylated surfactants has the average formula

$$[(R^4O)_3SiO]_2\overset{R^3}{\overset{|}{Si}}(OC_2H_3R^2)_c(OC_3H_6)_dOT \qquad \mathrm{III}$$

where R^2 and R^3 are as defined above, each R^4 group is independently a monovalent hydrocarbyl radical with the proviso that at least a majority of the R^4 groups are sterically hindered alkyl radicals having at least three carbon atoms, c is at least four, d is greater than or equal to zero, with the further proviso that c has a sufficient value and d is small enough so that a cured composition of the invention has the desired three minute water contact angle, and T is hydrogen, a monovalent alkyl or alkenyl radical, or a group of the formula $-Si(R^3)[OSi(OR^4)_3]_2$. Preferably in compounds of Formula III, R^2 is hydrogen, R^3 and T are $-CH_3$, R^4 is sec-butyl, c is five or more and d is zero. Representative ethoxylated surfactants of Formula III are described in the above-mentioned Olin Corp. product literature and in U.S. Patent Nos. 4,160,776, 4,226,794, and 4,337,168. At least one such surfactant is experimentally available from Olin Corp. as a "SILFAC" polyethoxylated silicate cluster compound bearing the experimental designation "SILFAC 12M".

[0023] An additional preferred class of ethoxylated surfactants has the average formula

$$(R^4O)_3Si(OC_2H_3R^2)_e(OC_3H_6)_fOT^1 \qquad \text{IV}$$

where R^2 and R^4 are as defined above, e is at least four, f is greater than or equal to zero, with the further proviso that e has a sufficient value and f is small enough so that a cured composition of the invention has the desired three minute water contact angle, and T^1 is hydrogen, a monovalent alkyl or alkenyl radical, or a group of the formula $-Si(OR^4)_3$. Such ethoxylated surfactants are believed to be novel and their preparation is described in more detail below. Preferably in compounds of Formula IV, R^2 is hydrogen, R^4 is sec-butyl, e is ten to 20, f is zero and T^1 is $-Si(\text{sec-butoxy})_3$.

[0024] Suitable ethoxylated surfactants containing perfluoroalkyl solubilizing groups are described in U.S. Patent No. 2,915,544. A preferred class of such ethoxylated surfactants has the average formula

$$Rf[Q(C_2H_3R^2O)_h(C_3H_6O)_iR^3]_{1 \text{ or } 2} \qquad \text{V}$$

where R^2 and R^3 are as defined above, Rf is a fluorinated, monovalent or divalent, aliphatic, preferably saturated organic radical containing at least four carbon atoms and at least a terminal perfluoromethyl group, Q is a polyvalent (e.g., divalent) hydrocarbylene linking group (e.g., $-C_2H_4-$, or $-SO_2NR-$ where R is as defined above), h is greater than or equal to one, and i is greater than or equal to zero, with the proviso that h has a sufficient value and i is small, enough so that a cured composition of the invention has the desired three minute water contact angle.

[0025] The surfactant used in the present invention can also be a cationic or amphoteric fluorosurfactant. Such fluorosurfactants contain at least one perfluoroalkyl solubilizing group Rf where Rf is as defined above. The cationic fluorosurfactants contain at least one cationogenic group which is the radical of a base having an ionization constant in water at 25°C of at least about 10^{-6}. The amphoteric fluorosurfactants contain at least one such cationogenic group and at least one anionogenic group which is the radical of an acid having an ionization constant in water at 25°C of at least about 10^{-6}. Suitable fluorosurfactants are described, for example, in U.S. Patent No. 4,484,990.

[0026] The compositions used in the invention contain sufficient surfactant so that a cured composition of the invention has the desired three minute water contact angle. As pointed out above, when the amount of surfactant is increased, the three minute water contact angle generally decreases. As the amount of surfactant is increased further, the three minute contact angle reaches a minimum threshold value which does not decrease significantly with the use of additional surfactant. In general, a preferred amount of surfactant is an amount sufficient to provide a three minute water contact angle having such minimum threshold value. This preferred amount of surfactant also depends upon the particular curable silicone prepolymer chosen, the particular surfactant chosen, and the amounts and types of other adjuvants present in the compositions of the invention. Expressed on a weight basis, an effective amount of surfactant preferably is below about 30 weight percent, based on the total weight of the composition. More preferably, the amount of surfactant is about 0.25 to five weight percent, and most preferably about 0.5 to two weight percent.

[0027] The compositions used in the invention are mixed packaged and stored like conventional curable silicone compositions. In two-part compositions, the surfactant usually can be present in either part of the composition, or in both parts of the composition. However, where the surfactant may tend to react with either part of the composition (e.g., if the surfactant contains one or more Si-H groups, and will be used in an addition cure polysiloxane), then the surfactant should be added only to a part of the composition with which it will not itself react. Mixtures of more than one surfactant can be used if desired.

[0028] The compositions used in the invention can also contain adjuvants of the type customarily employed in curable silicone compositions. Such adjuvants include crosslinking agents, catalysts, fillers, pigments, reinforcing agents, plasticizers and the like.

[0029] The invention is illustrated in the following examples, in which all parts and percentages are by weight unless otherwise indicated. Because the examples are merely illustrative, they are not to be construed as limiting the scope of the invention.

EXAMPLE 1

[0030] Several surfactants were evaluated in a two-part addition cure vinylpolysiloxane impression material formulation. Each surfactant was added at a level of one percent to both parts of the formulation. The two parts were then combined in equal proportions, mixed rapidly, poured into a cylindrical metal mold 19mm in diameter x 1mm in thickness sandwiched between two glass microscope slides, and allowed to cure for ten minutes at room temperature. A drop of distilled water was carefully placed on the cured surface and the contact angle formed by the drop was measured using a goniometer 30 seconds and three minutes after placement of the water drop. Set out below in TABLE I are the run number, surfactant, and measured water contact angles for each composition.

TABLE I

Run no.	Surfactant	Water contact angle	
		30 sec.	3 min.
1	None (control)	100°	99°
2	Polyalkylene oxide modified polymethylsiloxane ("Silwet L-77", Union Carbide Corp.)	9°	6°
3	Polyalkylene oxide modified polymethylsiloxane ("Silwet L-7600", Union Carbide Corp.)	97°	60°
4	Polyalkylene oxide modified polymethylsiloxane ("Silwet L-7602", Union Carbide Corp.)	92°	60°
5	$[(\text{sec-butoxy})_3SiO]_2Si(CH_3)(OC_2H_4)_{12}OCH_3$ ("SILFAC 12M", Olin Corp.)	36°	22°
6	$C_8F_{17}SO_2N(C_2H_5)C_2H_4O(C_3H_6O)_8H$	60°	55°
7	$C_8F_{17}SO_2N(C_2H_5)(C_2H_4O)_7H$	29°	20°
8	$C_8F_{17}SO_2N(C_2H_5)(C_2H_4O)_{14}H$	78°	26°
9	$C_8F_{17}SO_2NHC_3H_6N^+(CH_3)_3I^-$	102°	40°
10	$C_6F_{13}SO_2N(CH_2CHOHCH_2SO_3^-)C_3H_6N^+(CH_3)_2C_2H_4OH$ (1)	72°	64°
11	$C_8F_{17}SO_2N(C_2H_5)(CH_2)_2OCO(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$	82°	63°

(1) Evaluated at one % solids, using a 25 percent solution in $C_4H_9OC_2H_4OC_2H_4OH$.

[0031] The above example shows the useful improvement in water wettability obtained using the compositions of the invention. The composition of Run no. 2 was particularly effective. Slow cure (set) times were observed for the compositions of Run Nos. 9 and 11.

COMPARATIVE EXAMPLE 1

[0032] One percent (except where noted) additions of several comparison materials were evaluated in the impression material formulation of EXAMPLE 1. Set out below in TABLE II are the run number, comparison material, and measured water contact angles far each composition.

TABLE II

Run no.	Comparison material	Water contact angle	
		30 sec.	3 min.
1	Polyalkylene oxide modified polymethysiloxane ("Silwet L-720", Union Carbide Corp.)	94°	90°
2	Polyalkylene oxide modified polymethysiloxane ("Silwet L-7002", Union Carbide Corp.)	97°	97°
3	$CH_3Si[OSi(sec\text{-}butoxy)_3]_3$ ("Silicate Cluster 102", Olin Corp.)	--	105°(1)
4	$CH_3(OC_2H_4)_{7.2}OH$	--	76°(1)
5	$CH_3(OC_2H_4)_{7.2}OH$(2)	--	76°(1)
6	Sodium lauryl sulfate ("Duponol ME", E.I. duPont de Nemours & Co.)	91°	88°
7	Organic phosphate ester, free acid ("Gafac PE-510", GAF Corp.)	89°	74°
8	Fatty amide ("Antaron FC-34", GAF Corp.)	90°	82°
9	Polyethoxylated fatty alcohol ("Emulphor AM-310", GAF)	33°	28°
10	$(H_3C)_3CCH_2C(CH_3)_2C_6H_4(OC_2H_4)_{9\text{-}10}OH$ ("Triton X-100", Rohm & Haas)	81°	64°
11	$C_9H_{19}C_6H_4O(C_2H_4)_{9\text{-}10}OH$ ("Igepal CO-630", GAF)	68°	46°
12	Butoxypolypropyleneoxypolyethyleneoxyethanol ("Tergitol XD", Union Carbide Corp.)(3)	55°	50°
13	30:70 Copolymer of $C_8F_{17}SO_2N(CH_3)C_2H_4OCOC(CH_3)=CH_2$ and $CH_3O(C_2H_4O)_{16}COCH=CH_2$	103°	101°
14	$C_8F_{17}SO_3K$	89°	88°
15	$C_7F_{15}COONH_4$	90°	85°

(1) Water contact angle measured at equilibrium. The three minute water contact angle would be the same or only slightly different.

(2) Evaluated at ten percent comparision material rather than one percent.

(3) Evaluated at two percent surfactant instead of at one percent. When evaluated at one percent, the 30 second water contact angle was 86° and the three minute water contact angle was 76°.

[0033] The materials of Run nos. 1 and 2 did not have a sufficient number of ethyleneoxy groups or had too many propyleneoxy groups. The materials of Run nos. 3, 6 through 8, 15 and 16 were not ethoxylated surfactants, cationic fluorosurfactants, or amphoteric fluorosurfactants. The materials of Run nos. 4 through 12 did not contain siloxane or perfluoroalkyl solubilizing groups. The material of Run no. 14 was a waxy solid.

EXAMPLE 2

[0034] A conventional two-part condensation cure silicone impression material ("Citricon" Dental Impression Resin, Kerr Division of Sybron Corp.) was made hydrophilic by the addition of one percent $[(sec\text{-}butoxy)_3SiO]_2Si(CH_3)(OC_2H_4)_{12}OCH_3$ to each part. The three minute water contact angle was reduced from 98° without surfactant to 28° with surfactant.

EXAMPLE 3

[0035] Varying amounts of $[(sec\text{-}butoxy)_3SiO]_2Si(CH_3)(OC_2H_4)_{12}OCH_3$ were added to both parts of the impression material formulation of EXAMPLE 1. The resulting compositions were cured and evaluated using the method of EXAMPLE 1, with water contact angles being measured at equilibrium rather than at three minutes. The water contact angles at thre minutes typically would be the same or only slightly different. Set out below in TABLE III are the run number, percent surfactant, and equilibrium water contact angle for each composition.

TABLE III

Run no.	% Surfactant	Equilibrium water contact angle
1	0	100°
2	0.125	102°
3	0.25	48°
4	0.5	34°
5	1.0	32°
6	2.0	27°
7	15.0	26°
8	30.0	21°

[0036] The above example illustrates the effect of variation in the amount of surfactant.

EXAMPLE 4

[0037] The composition of Run no. 6 of EXAMPLE 3 was cured in a two mm deep split mold made by stacking two of the one mm deep molds used in EXAMPLE 3. After curing the composition, the upper half of the mold was removed and the cured composition then sliced in half at the mold parting line using a razor blade. A water contact angle measurement was quickly performed on a sliced surface of the sample. At equilibrium, its water contact angle was 25°, compared to 27° for Run no. 6 of EXAMPLE 3.

[0038] The above example illustrates that the interior of a cured composition of the invention is hydrophilic.

EXAMPLE 5

[0039] Varying amounts of the ethoxylated surfactant "Silwet L-77" were added to both parts of the impression material formulation of EXAMPLE 1. The resulting compositions were cured and evaluated using the method of EXAMPLE 1. Set out below in TABLE IV are the run number, percent surfactant, and three minute water contact angle for each composition.

TABLE IV

Run no.	% Surfactant	3 Minute water contact angle
1	0	100°
2	0.25	67°
3	0.30	45°
4	0.75	12°
5	1.00	9°

[0040] The above example also illustrates the effect of variation in the amount of surfactant.

EXAMPLE 6

[0041] A series of silicate "cluster" surfactants having the following average formula were synthesized using the method shown in Example 1 of U.S. Patent No. 4,226,794:

$$[(\text{sec-butoxy})_3\text{SiO}]_2\overset{\displaystyle R}{\overset{|}{\text{Si}}}(\text{OC}_2\text{H}_4)_n\text{O}\overset{\displaystyle R}{\overset{|}{\text{Si}}}[\text{OSi}(\text{sec-butoxy})_3]_2.$$

[0042] One percent of each of these surfactants was added to both parts of the impression material formulation of EXAMPLE 1. Set out below in TABLE V are the run number, identity of R and n, and the equilibrium water contact angle for each composition.

TABLE V

Run no.	R	n	Equilibrium water contact angle
1	H-	13.2	52°
2	CH_3-	3.0	92°
3	CH_3-	8.7	65°
4	CH_3-	13.2	56°
5	CH_2=CH-	13.2	66°
6	CH_2=CH-	34.6	59°

[0043] An additional series of silicate "cluster" surfactants of the following average formula was synthesized using the method shown in Example 2 of U.S. Patent No. 4,160,776:

$$[(\text{sec-butoxy})_3\text{SiO}]_2\overset{\displaystyle R}{\overset{|}{\text{Si}}}(\text{OC}_2\text{H}_4)_n\text{OCH}_3.$$

[0044] One percent of each of these surfactants was added to both parts of the impression material formulation of EXAMPLE 1. Set out below in TABLE VI are the run number, identity of R and n, and the equilibrium water contact angle for each composition.

TABLE VI

Run no.	R	n	Equilibrium water contact angle
1	H-	7.2	39°
2	CH_3-	7.2	31°
3	CH_3-	11.8	32°
4	CH_3-	16.3	37°
5	CH_2=CH-	2.0	88°
6	CH_2=CH-	7.2	49°
7	CH_2=CH-	11.8	28°
8	CH_2=CH-	42.5	100°

[0045] The above example shows the effect variations in structure have upon the hydrophilicity of a cured compo-

sition of the invention.

EXAMPLE 7

[0046] Tri(sec-butoxy)chlorosilane was prepared according to the procedure described in Schott, G., Englebrecht, L., and Holdt, H.J., Z. anorg. allg. Chem., 459, 177-186 (1979). A 56.5 g portion of the resulting product was added dropwise to a stirred solution of 60 g of a polyethyleneglycol having the average formula $HO(C_2H_4O)_{13.2}H$ ("Carbowax 600", Union Carbide Corp.) and 16 g pyridine in 300 ml toluene. The resulting mixture was heated to 70°C for two hours, then allowed to cool to room temperature and filtered to remove pyridine hydrochloride. Toluene was removed from the mixture using a rotary evaporator. Final traces of toluene and unreacted pyridine were removed under high vacuum (10^{-2} Torr). The product was a clear, colorless to faint yellow fluid. NMR and IR analyses were consistent with the average structure $(sec\text{-}butoxy)_3SiO(C_2H_4O)_{13.2}Si(sec\text{-}butoxy)_3$. Using ^1H NMR analysis with $CDCl_3$ as solvent, delta values were 0.90(18H,d,-$CHCH_3$), 1.17 (18H,t,-CH_2CH_3), 1.45 (12H,q,-CH_2CH_3), 3.61 (53H,s,OCH_2CH_2), and 3.87 (6H,-CH). Using IR analysis, absorption peaks occurred at 2898, 1485, 1379, 1351, 1330, 1299, 1258, 1117, 1058, 1018, 960, 862, 816 and 735 cm^{-1}.

[0047] When one percent of this novel ethoxylated surfactant was added to both parts of the impression material formulation of EXAMPLE 1, the cured composition had 30 second and three minute water contact angles of 44° and 32°, respectively.

EXAMPLE 8

[0048] Using the method of EXAMPLE 7, and substituting a variety of alkoxylated linear alcohols or diols for the polyethyleneglycol used in EXAMPLE 7, a series of novel alkoxylated surfactants having the average formula $(R^4O)_3Si(OC_2H_4)_e(OC_3H_6)_fOT^1$ were synthesized. Using the method of EXAMPLE 1, one percent of each of these surfactants was added to both parts of the impression material formulation of EXAMPLE 1. Set out below in TABLE VII are the run number, identity of R^1, e, f and T^1, and the equilibrium water contact angle for each composition.

TABLE VII

Run no.	R^4	e	f	T^1	Equilibrium water contact angle
1	sec-butyl	2	0	$-CH_3$	90°
2	sec-butyl	7.2	0	$-CH_3$	56°
3	sec-butyl	11.8	0	$-CH_3$	72°
4	sec-butyl	16.3	0	$-CH_3$	84°
5	sec-butyl	42.5	0	$-CH_3$	98°
6	sec-butyl	3	0	T'(1)	76°
7	sec-butyl	6.4	0	T'	63°
8	sec-butyl	8.7	0	T'	57°
9	sec-butyl	13.2	0	T'	36°
10	sec-butyl	22.3	0	T'	59°
11	sec-butyl	0	16.9	T'	71°
12	sec-butyl	0	18.8	T'	66°
13	sec-butyl	0	34.2	T'	73°
14	sec-butyl	0	51.4	T'	76°
15	(2)	7.2	0	$-CH_3$	44°
16	(2)	16.3	0	$-CH_3$	59°
17	(2)	13.2	0	T''(3)	85°
18	(2)	22.3	0	T''	76°

(1) T' = $-Si(sec\text{-}butoxy)_3$.
(2) Two sec-butoxy groups and one allyloxy group were attached to the Si atom shown in the formula.
(3) T'' = $-Si(sec\text{-}butoxy)_2(allyloxy)$.

[0049] The above example shows several novel surfactants, and the effect variation in their structure has upon the hydrophilicity of a cured composition as used in the invention.

EXAMPLE 9

[0050] Three curable silicone compositions were formulated as in EXAMPLE 1, using one percent $[(sec\text{-}butoxy)_2SiO]_2Si(CH_3)(OC_2H_4)_{12}OCH_3$ in the catalyst-containing portion, non-catalyst-containing ("base") portion or both portions of the formulation. The cure time of each composition was measured at 24°C (using a "Monsanto" oscillating disk rheometer) immediately after preparing the compositions, and after aging the compositions for seven days at 60°C. The results are set out below in TABLE VIII.

TABLE VIII

Surfactant added to		Cure time, minutes:seconds	
Catalyst	Base	Unaged	Aged 7 days @ 60°C
No	No	5:15(1)	4:45(1)
Yes	No	5:00	4:55
No	Yes	4:34	4:30
Yes	Yes	4:55	4:50

(1) Average of several runs.

[0051] Comparable results were obtained when this example was repeated using the ethoxylated surfactant "Silwet L-77".

[0052] The above example demonstrates the excellent storage stability which can be obtained with these compositions.

EXAMPLE 10

[0053] The composition of Run no. 5 of EXAMPLE 1 was prepared without silica fillers. The equilibrium water contact angle of the cured composition was 28°, compared to 32° when fillers were included.

[0054] This example illustrates that the use of filler did not materially affect hydrophilicity.

EXAMPLE 11

[0055] The composition of Run no. 4 of EXAMPLE 5 was cured and washed in cold running tap water for two days. The measured water contact angle (as observed using an optical comparator) increased from 20-23° before washing to 60-63° after washing. Schlieren patterns could be observed within the water drop when it was placed on the cured silicone surface. This example indicates that the surfactant may have migrated from the silicone into the wash water and into the water drop.

EXAMPLE 12

[0056] The composition of Run no. 4 of EXAMPLE 5 was extruded in a thin stream into a tray of water. The extrudate tended to maintain its shape underwater. A composition prepared without surfactant tended to "ball-up" underwater, perhaps in order to minimize its exposed surface area. This example indicates that the compositions of the invention may yield impressions with improved accuracy in submerged fields, such as impressions of the gingival sulcus made in the presence of crevicular fluids.

EXAMPLE 13

[0057] The composition of Run no. 4 of EXAMPLE 5 was used to make an impression of a grooved aluminum block according to the procedure of American Dental Association Specification No. 19. The composition produced an excellent impression which passed the specification. It also passed if the aluminum block was flooded with water before taking the impression. A composition prepared without surfactant passed if the aluminum block was dry but failed if the block was wet.

EXAMPLE 14

[0058] Several silicone impression material formulations and comparison polyether impression material formulations were cast in a rectangular prismatic mold to form a cast bar 57mm long x 20mm wide x four mm thick. The mold had been previously scribed with two marks across its long dimension, spaced 50mm apart. These marks were reproduced in the cast bar. Each bar was stored at room temperature and 32 percent or 100 percent relative humidity for 24 hours, then removed and measured to determine if th spacing between the scribed marks had changed. Set out below in TABLE IX are the run number, impression material, and the measured dimensional change at each relative humidity.

TABLE IX

Run no.	Impression material	Dimensional change	
		32% R.H.	100% R.H.
1	Addition cure vinylpolysiloxane	+0.02%	+0.21%
2	Run no. 1 +0.75% "Silwet L-77"[(1)]	-0.07%	+0.22%
3	Polyether[(2)]	+0.08%	+0.64%
4	Polyether[(3)]	-0.04%	+0.75%

(1) Average of three samples.
(2) "Impregum Impression Material Type 1", Premier Dental Products.
(3) "Polyjel", L. D. Caulk Company.

[0059] The above example illustrates the excellent dimensional stability of compositions of the invention even when stored under conditions of high humidity.

EXAMPLE 15

[0060] A two-part addition cure vinylpolysiloxane impression material formulation containing 0.375% "Silwet L-77" surfactant was used to make impressions of the oral tissue of ten patients. Most patients could detect a slight taste, but none found it objectionable. Those patients that noticed a taste judged it to be much better than the taste of rubber-base or polyether impression materials. An additional impression was made of the oral tissue of a patient who had previously experienced a severe allergic reaction to a commercial polyether impression material. She detected no taste and did not experience any allergic reaction or other adverse symptoms.

EXAMPLE 16

[0061] A two-part addition cure vinylpolysiloxane impression material formulation was used to make impressions of the oral tissue of three patients. Excellent detail reproduction was obtained.

EXAMPLE 17

[0062] A typical full crown preparation was made on the upper left lateral incisor of a "Typodont" dental model. Two custom impression trays were prepared by lining the trays with the hydrophilic impression material of EXAMPLE 15 or with a corresponding non-hydrophilic impression material prepared without ethoxylated surfactant. Two final impressions were taken by lining these custom trays with the hydrophilic impression material of Run No. 5 of EXAMPLE 1 or with the non-hydrophilic impression material of Run No. 1 of EXAMPLE 1, respectively. Models of the cured impressions were poured using "Vel-Mix Stone" (Kerr Division of Sybron Corp.). The model made from the hydrophilic impression materials was evaluated by three consulting dentists, and regarded by each as superior to the model made from the non-hydrophilic impression materials, especially in detail reproduction.

[0063] Comparable results were obtained when this example was repeated by taking impressions of the oral tissue of several human patients. The observed superiority of the models made from the hydrophilic impression materials was especially apparent for impressions made under moist field conditions.

Claims

1. Use, as a dental impression material of a curable room temperature vulcanizing silicone composition said composition comprising a mixture of (a) curable silicone prepolymer and (b) surfactant selected from the group consisting of (i) ethoxylated nonionic surface active agents containing one or more siloxane or perflucroalkyl solubilizng groups and (ii) cationic or amphoteric fluorochemical surface active agents, in which, when the surfactant is a cationic surfactant, it contains at least one cationogenic group which is the radical of a base having an ionization constant in water at 25°C of at least about 10^{-6}, and, when it is an amphoteric surfactant, it contains at least one such cationogenic group and also at least one anionogenic group which is the radical of an acid having an ionization constant in water at 25°C of at least about 10^{-6}, said surfactant being present in sufficient amount and said ethoxylated nonionic surface active agent, if present, containing sufficient ethyleneoxy groups so that said composition, when

cured, has a three minute water contact angle below 65°, and said surfactant being capable of migration throughout the cured silicone composition and into adjacent fluids.

2. Use according to claim 1, charact rised in that said curabl silicone prepolymer comprises a two-part additi n cure or condensation cure polysiloxane.

3. Use according to claim 1, characterised in that said agent contains at least three unsubstituted or hydroxyalkyl-substituted ethyleneoxy groups.

4. Use according to claim 3, characterized in that said agent contains five to fifteen unsubstituted ethyleneoxy groups.

5. Use according to claim 1 characterized by comprising surfactant having the following average formulas I, II or III:

$$R-\underset{R}{\overset{R}{Si}}O-\left[\underset{R}{\overset{R}{Si}}O\right]_x-\left[\underset{R^1O(C_2H_3R^2O)_a(C_3H_6O)_bR^3}{\overset{R}{Si}}O\right]_y-\underset{R}{\overset{R}{Si}}-R \qquad \text{I}$$

$$RSi[(O\underset{R}{\overset{R}{Si}})_x(OC_2H_3R^2)_a(OC_3H_6)_bOR^3]_3 \qquad \text{II}$$

$$[(R^4O)_3SiO]_2\overset{R^3}{Si}(OC_2H_3R^2)_c(OC_3H_6)_dOT \qquad \text{III}$$

wherein each R is independently a monovalent hydrocarbyl radical, R^1 is a divalent hydrocarbylene radical, each R^2 is independently hydrogen or a lower hydroxyalkyl radical, R^3 is hydrogen or a monovalent hydrocarbyl radical, each R^4 group is independently a monovalent hydrocarbyl radical with the proviso that at least a majority of the R^4 groups are sterically hindered alkyl radicals having at least three carbon atoms, x and b are independently greater than or equal to zero, y and a are independently greater than or equal to one, c is at least 4, d is greater than or equal to zero and T is a monovalent alkyl or alkenyl radical or a group of the formula $-Si(R^2)[OSi(OR^4)_3]_2$ with the proviso that a and c have a sufficient value and b and d are small enough so that said composition, when cured, has a three minute water contact angle below 65°.

6. Use according to claim 5 characterized in that R, R^3 and T are $-CH_3$, R^1 is $-C_3H_6-$, R^2 is hydrogen, R^4 is sec-butyl, x is zero or one, y is one to five, a is five to 20, b and d are zero and c is 5 or more.

7. Use according to claim 6 characterized in that said curable silicone prepolymer comprises a two part addition cure polysiloxane, said surfactant has said formula I, y is one or two, a is about seven, and said contact angle is below 30°.

8. Use according to claim 1 characterised by comprising surfactant having the average formula

$$Rf[Q(C_2H_3R^2O)_h(C_3H_6O)_iR^3]_{1\ \text{or}\ 2}$$

wherein Rf is a fluorinated, monovalent or divalent, aliphatic organic radical containing at least four carbon atoms and at least a terminal perfluoromethyl group, Q is a polyvalent hydrocarbylene linking group, each R^2 is independently hydrogen or a lower hydroxyalkyl radical, R^3 is hydrogen or a monovalent hydrocarbyl radical, h is greater than or equal to one, and i is greater than or equal to zero, with the proviso that h has a sufficient value and i is small

enough so that said composition, when cured, has a three minute water contact angle below 65°.

9. Use according to claim 1 characterized by comprising a cured mixture of the curable silicon composition defined in any one of claims 1-8, said cured composition comprising a negativ mould of oral tissue, and having semipermanent hydrophilicity.

Patentansprüche

1. Verwendung einer bei Zimmertemperatur härtbaren, vulkanisierenden Silikonmasse als Zahnabdruckmaterial, wobei die Masse umfasst:

   ein Gemisch aus (a) einem härtbaren Silikonpräpolymer und (b) einem Netzmittel, ausgewählt aus

   (i) ethoxylierten nicht ionischen grenzflächenaktiven Stoffen, die ein oder mehr solubilisierende Siloxan- oder Perfluoralkylreste enthalten, und
   (ii) kationischen oder amphoteren fluorchemischen grenzflächenaktiven Stoffen,

   in dem das Netzmittel, wenn es ein kationisches Netzmittel ist, wenigstens einen kationogenen Rest enthält, der der Rest einer Base mit einer Dissoziationskonstante in Wasser bei 25 °C von wenigstens etwa 10^{-6} ist, und es, wenn es ein amphoteres Netzmittel ist, wenigstens einen solchen kationogenen Rest und auch wenigstens einen anionogenen Rest, der der Rest einer Säure mit einer Dissoziationskonstante in Wasser bei 25 °C von wenigstens etwa 10^{-6} ist, enthält,
   wobei das Netzmittel in genügender Menge vorhanden ist und der ethoxylierte nicht ionische grenzflächenaktive Stoff, falls vorhanden, genügend Ethylenoxygruppen enthält, so dass die Masse, wenn sie gehärtet ist, einen Drei-Minuten-Wasserbenetzungswinkel unterhalb von 65° aufweist und das Netzmittel durch die gesamte gehärtete Silikonmasse und in angrenzende Fluide wandern kann.

2. Verwendung nach Anspruch 1, dadurch gekennzeichnet, dass das härtbare Silikonpräpolymer ein zweikomponentiges Additionshärtungs- oder Kondensationshärtungspolysiloxan umfasst.

3. Verwendung nach Anspruch 1, dadurch gekennzeichnet, dass der Stoff wenigstens drei unsubstituierte oder hydroxyalkyl-substituierte Ethylenoxygruppen umfasst.

4. Verwendung nach Anspruch 3, dadurch gekennzeichnet, dass der Stoff 5 bis 15 unsubstituierte Ethylenoxygruppen enthält.

5. Verwendung nach Anspruch 1, dadurch gekennzeichnet, dass sie ein Netzmittel mit den folgenden durchschnittlichen Formeln I, II oder III umfasst:

$$R_3Si\text{-}O\text{-}[SiR_2O]_x\text{-}[SiR(R^1O(C_2H_3R^2O)_a(C_3H_6O)_bR^3)O]_y\text{-}SiR_3 \qquad \text{I}$$

$$RSi[(OSiR_2)_x(OC_2H_3R^2)_a(OC_3H_6)_bOR^3]_3 \qquad \text{II}$$

$$((R^4O)_3SiO)_2Si(R^3)(OC_2H_3R^2)_c(OC_3H_6)_dOT \qquad \text{III}$$

wobei jeder Rest R unabhängig ein einwertiger Kohlenwasserstoffrest ist, R^1 ein zweiwertiger Kohlenwasserstoffrest ist, jeder Rest R^2 unabhängig ein Wasserstoffatom oder ein Niederhydroxyalkylrest ist, R^3 ein Wasserstoffatom oder ein einwertiger Kohlenwasserstoffrest ist, jeder Rest R^4 unabhängig ein einwertiger Kohlenwasserstoffrest ist, mit der Maßgabe, dass wenigstens eine Mehrzahl der Reste R^4 sterisch gehinderte Alkylreste mit wenigstens drei Kohlenstoffatomen ist,
x und b unabhängig größer als oder gleich 0 sind, y und a unabhängig größer als oder gleich 1 sind, c wenigstens 4 ist, d größer als oder gleich 0 ist und T ein einwertiger Alkyl- oder Alkenylrest oder ein Rest der Formel -$Si(R^2)[OSi(OR^4)_3]_2$ ist, mit der Maßgabe, dass a und c einen ausreichenden Wert haben und b und d klein genug sind, so dass die Masse, wenn sie gehärtet ist, einen Drei-Minuten-Wasserbenetzungswinkel unterhalb von 65° aufweist.

6. Verwendung nach Anspruch 5, dadurch gekennzeichnet, dass R, R^3 und T für -CH_3 stehen, R^1 für -C_3H_6- steht, R^2 ein Wasserstoffatom ist, R^4 eine sec-Butylgruppe ist, x 0 oder 1 ist, y 1 bis 5 ist, a 5 bis 20 ist, b und d 0 sind und c 5 oder mehr ist.

7. Verwendung nach Anspruch 6, dadurch gekennzeichnet, dass das härtbare Silikonpräpolymer ein zweikomponentiges Additionshärtungspolysiloxan umfasst, das Netzmittel die Formel I aufweist, y 1 oder 2 ist, a etwa 7 ist und der Benetzungswinkel unterhalb von 30° liegt.

8. Verwendung nach Anspruch 1, dadurch gekennzeichnet, dass sie ein Netzmittel mit der durchschnittlichen Formel umfasst:

$$Rf[Q(C_2H_3R^2O)_h(C_3H_6O)_iR^3]_{1 \text{ or } 2}$$

wobei Rf ein fluorierter, ein- oder zweiwertiger, aliphatischer organischer Rest ist, der wenigstens vier Kohlenstoffatome und wenigstens eine endständige Perfluormethylgruppe enthält, Q ein mehrwertiger verknüpfender Kohlenwasserstoffrest ist, jeder Rest R^2 unabhängig ein Wasserstoffatom oder ein Niederhydroxyalkylrest ist, R^3 ein Wasserstoffatom oder ein einwertiger Kohlenwasserstoffrest ist, h größer als oder gleich 1 ist und i größer als oder gleich 0 ist, mir der Maßgabe, dass h einen ausreichenden Wert hat und i klein genug ist, so dass die Masse, wenn sie gehärtet ist, einen Drei-Minuten-Wasserbenetzungswinkel unterhalb von 65° aufweist.

9. Verwendung nach Anspruch 1, dadurch gekennzeichnet, dass sie ein gehärtetes Gemisch der härtbaren Silikonmasse nach einem der Ansprüche 1 bis 8 umfasst, wobei die gehärtete Masse einen negativen Abguss von oralem Gewebe umfasst und semipermanente Hydrophilie besitzt.

Revendications

1. Utilisation, comme matériau d'empreinte dentaire, d'une composition de silicone de vulcanisation à température ambiante durcissabl , ladite c mposition comprenant un mélange (a) de prépolymère de silicone durcissable et (b) d'agent tensioactif choisi dans le groupe comprenant (i) les agents tensioactifs non ioniques éthoxylés contenant un ou plusieurs groupes de solubilisation de siloxane ou perfluoroalkyle et (ii) les agents tensioactifs fluorochimiques cationiques ou amphotères, dans laquelle, lorsque l'agent tensioactif est un agent tensioactif cationique, il contient au moins un groupe cationogénique qui est le radical d'une base ayant une constante d'ionisation dans l'eau à 25°C d'au moins environ 10^{-6}, et, lorsqu'il est un agent tensioactif amphotère, il contient au moins un tel groupe cationogénique et également au moins un groupe anionogénique qui est le radical d'un acide ayant une constante d'ionisation dans l'eau à 25°C d'au moins environ 10^{-6}, ledit agent tensioactif étant présent en quantité suffisante et ledit agent tensioactif non ionique éthoxylé, si présent, contenant des groupes éthylénoxy suffisants de telle sorte que ladite composition, lorsque durcie, ait un angle de contact à l'eau après trois minutes en dessous de 65°, et l'agent tensioactif précité pouvant migrer à travers la totalité de la composition de silicone durcie et dans des fluides adjacents.

2. Utilisation suivant la revendication 1, caractérisée en ce que le prépolymère de silicone durcissable susdit comprend un polysiloxane de durcissement par addition ou de durcissement par condensation à deux parties.

3. Utilisation suivant la revendication 1, caractérisée en ce que l'agent susdit contient au moins trois groupes éthylénoxy non substitués ou hydroxyalkyl-substitués.

4. Utilisation suivant la revendication 3, caractérisée en ce que ledit agent contient cinq à quinze groupes éthylénoxy non substitués.

5. Utilisation suivant la revendication 1, caractérisée en ce qu'elle comprend un agent tensioactif ayant les formules moyennes I, II ou III suivantes :

$$R_3SiO\left[R_2SiO\right]_x\left[\underset{R^1O(C_2H_3R^2O)_a(C_3H_6O)_bR^3}{\overset{R}{|}}\!\!SiO\right]_y SiR_3 \qquad \text{I}$$

$$RSi\left[\left(O\underset{R}{\overset{R}{Si}}\right)_x(OC_2H_3R^2)_a(OC_3H_6)_bOR^3\right]_3 \qquad \text{II}$$

$$\left[(R^4O)_3SiO\right]_2\overset{R^3}{Si}(OC_2H_3R^2)_c(OC_3H_6)_dOT \qquad \text{III}$$

dans lesquelles chaque R représente indépendamment un radical hydrocarbyle monovalent, R^1 est un radical hydrocarbylène divalent, chaque R^2 représente indépendamment de l'hydrogène ou un radical hydroxyalkyle inférieur, R^3 est de l'hydrogène ou un radical hydrocarbyle monovalent, chaque groupe R^4 représente indépendamment un radical hydrocarbyle monovalent à la condition qu'au moins une majorité des groupes R^4 représentent des radicaux alkyle à empêchement stérique comportant au moins trois atomes de carbone, x et b sont indépendamment supérieurs ou égaux à zéro, y et a sont indépendamment supérieurs ou égaux à un, c est égal à au moins 4, d est supérieur ou égal à zéro et T est un radical alkyle ou alcényl monovalent ou un groupe de la formule $-Si(R^2)[OSi(OR^4)_3]_2$ à la condition que a et c aient une valeur suffisante et que b et d soient suffisamment petits pour que la composition précitée, lorsque durcie, ait un angle de contact à l'eau après trois minutes en dessous de

65°.

6. Utilisation suivant la revendication 5, caractérisée en ce que R, R^3 et T représentent $-CH_3$, R^1 est $-C_3H_6$, R^2 est de l'hydrogène, R^4 est du sec-butyle, x est égal à zéro ou un, y vaut de un à cinq, a vaut de 5 à 20, b et d sont égaux à zéro et c est égal à 5 ou plus.

7. Utilisation suivant la revendication 6, caractérisée en ce que le prépolymère de siliconne durcissable précité comprend un polysiloxane de durcissement par addition à deux parties, l'agent tensioactif précité a la formule I, y est égal à un ou deux, a vaut environ sept et l'angle de contact précité est en dessous de 30°.

8. Utilisation suivant la revendication 1, caractérisée en ce qu'elle comprend un agent tensioactif ayant la formule moyenne :

$$Rf[Q(C_2H_3R^2O)_h(C_3H_6O)_iR^3]_{1\ \text{ou}\ 2}$$

dans laquelle Rf est un radical organique aliphatique, monovalent ou divalent, fluoré, contenant au moins quatre atomes de carbone et au moins un groupe perfluorométhyle terminal, Q est un groupe de liaison hydrocarbylène polyvalent, chaque R^2 représente indépendamment de l'hydrogène ou un radical hydroxyalkyle inférieur, R^3 est de l'hydrogène ou un radical hydrocarbyle monovalent, h est supérieur ou égal à un et i est supérieur ou égal à zéro, à la condition que h ait une valeur suffisante et i soit suffisamment petit pour que la composition précitée, lorsque durcie, ait un angle de contact à l'eau après trois minutes en dessous de 65°.

9. Utilisation suivant la revendication 1, caractérisée en ce qu'elle comprend un mélange durci de la composition de silicone durcissable définie dans l'une quelconque des revendications 1 à 8, ladite composition durcie comprenant un moule négatif de tissu oral, et ayant une hydrophilicité semi-permanente.